

Terpolymerization of propene and ethene with carbon monoxide catalyzed by [PdCl₂(dppf)] in HCOOH–H₂O as a solvent [dppf = 1,1'-bis(diphenylphosphino)ferrocene]

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ABSTRACT

The [PdCl₂(dppf)] complex efficiently catalyzes the terpolymerization of propene and ethene with carbon monoxide in HCOOH–H₂O as a solvent, when H₂O concentration ranges between 50 and 65 molar %. The productivity, the melting temperature and the viscosity average molecular weight of the terpolymer depend on the propene concentration and on the reaction time.

The NMR analysis of the polymer composition indicates the presence along the chain mainly of ethene–CO units together with a low percent of propene–CO units.

A reaction mechanism is proposed and discussed.

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1. Introduction

Pd(II)-chelating diphosphine complexes efficiently catalyze the strictly alternating co- and ter-polymerization of CO with aliphatic 1-olefins, providing access to a new family of engineering thermoplastics named polyketones (PK) [1–3].

In contrast to the intensive efforts devoted to ethene (E)–carbon monoxide (ECO) copolymerization, much less has been reported on terpolymerization of two olefins with carbon monoxide [1–12], although industries have shown more interest for terpolymers than for copolymers, as documented by the high number of patents in this field. This is because the ECO copolymer is a highly crystalline material with high melting point (*T_m*), whereas the terpolymers have lower melting points, making them more easily processable [13–19]. As matter of fact, the first commercialized PK, was the propene (P)–ethene–CO (PECO) terpolymer (trade name CARILON® by Shell [20] and KETONEX® by BP [21]). Currently, several industries are showing renovated keen interest in these terpolymers, searching for new catalytic systems more efficient and selective in particular for applications in the field of lubricants (oligomers) and/or in the field of fibers (high molecular weight). In general, for

fiber production both high productivity of the catalyst and high average molecular weight of the polymer are required.

Among the main aspects that rule the Pd(II)-catalysis the nature of the chelating ligand, of the counter-anion and of the solvent plays a key role [1–3,22–25]. Methanol is the most used solvent in which case the counter-anions must be weakly coordinating in order to ensure high productivity.

We recently reported that by using reaction media such as H₂O–MeOH, H₂O–CH₃COOH or H₂O–HCOOH also Pd(II)-complexes having strongly coordinating ligands efficiently catalyze the reaction [26–30]. For example, we have found that the [PdCl₂(dppf)] complex efficiently catalyzes the terpolymerization with propene (P), 1-hexene (Hex), 1-decene (D) or styrene (S) with CO (5000 gPECO/(gPd h), 5600 gHexECO/(gPd h), 5650 gDECO/(gPd h) and 4100 gSECO/(gPd h), in MeOH as a solvent containing H₂O and TsOH as co-promoters [6].

In addition, it is reported that the CO–ethene copolymerization catalyzed by a cationic Pd(II)-dppf based catalyst, using MeOH as a solvent, gives PKs of low molecular weight, together with co-oligomers and other carbonylated products of even lower molecular weight such as dimethyl 4-oxoheptanoate, dimethyl succinate, methyl 4-oxohexanoate and methyl propanoate [31]. Under the same experimental conditions, but in CH₃COOH–H₂O as a solvent, we achieved a remarkable increase of the catalytic activity together with an increase of the average molecular weight [29].

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More recently, interesting results have been obtained in HCOOH–H₂O as a solvent in which the catalyst shows both a higher catalytic activity and a higher ECO molecular weight also using strongly coordinating counter anions. As matter of fact, we reported that the [PdCl₂(dppf)] complex in such a solvent efficiently catalyzes the ethene–CO (ECO) copolymerization leading to high molecular weight polymer with a productivity of 20,200 gECO/(gPd h), at 90 °C, 45 atm (CO/E = 1/1), and H₂O ca. 50 molar % [32]. It is worth to point out that both [Pd(OAc)₂(dppf)] and [PdCl₂(dppf)] are inactive in MeOH. This prompted us to extend the use of H₂O–organic acid as a solvent to the terpolymerization of ethene and another olefin with CO.

In this paper, we report on the catalytic activity of the [PdCl₂(dppf)] precursor in the PECO terpolymerization carried out in H₂O–HCOOH as a solvent. The effect of the operative conditions on the productivity and on the viscosity average molecular weight has been studied. A reaction mechanism has been also proposed and discussed.

2. Experimental

2.1. Reagents

Palladium(II) chloride was purchased from Engelhard Italy SRL; 1,1'-bis(diphenylphosphino)ferrocene (dppf), 1,1,1,3,3,3-hexafluoroisopropanol (99%), methanol (H₂O = 100 ppm) and CDCl₃ were Aldrich products. Carbon monoxide, ethene and propene were supplied by SIAD Company ('research grade', purity >99.9%).

The complex [PdCl₂(dppf)] was prepared as reported in literature [33].

2.2. Equipment

The catalyst precursor was weighted on a Sartorius Micro balance.

Gas-chromatographic analysis of the liquid phase was performed on a Hewlett Packard Model 5890, Series II chromatograph fitted with a HP1, 30 m × 0.35 μm × 0.53 μm column (detector: FID; carrier gas: N₂, 0.2 ml/min; oven: 50 °C (2 min) to 200 °C at 15 °C/min).

All the NMR spectra were recorded on a Bruker Avance 300 spectrometer by dissolving the polymers in a 1,1,1,3,3,3-hexafluoroisopropanol/CDCl₃ (10/1). The ¹³C NMR spectra of the polyketone were recorded using the Inverse ¹H-Gated Decoupling Technique.

FTIR spectra were recorded on a Nicolet Magna 750 instrument in KBr powder.

The melting temperatures of polymers have been determined on a Perkin Elmer Differential Scanning Calorimeter (mod. DSC 7) instrument.

2.3. Terpolymerization

The polymerizations were carried out by using a Hastelloy C autoclave of 280 mL provided with a four-blade self-aspirating turbine. In order to avoid contamination by metallic species because of corrosion of the internal surface of the autoclave, solvent and catalyst were contained in a ca. 150 mL Pyrex bottle, placed inside the autoclave. The free volume available to the liquid and to the gas phase was 250 mL. The gaseous monomers (E and CO) were supplied to the autoclave in the ratio 1/1 from a gas reservoir connected to the autoclave through a constant pressure regulator whereas the liquid monomer was mixed with the solvent before running the reactions.

Table 1
Most relevant ¹³C NMR and ¹H NMR signals for PECO terpolymer.

	¹ H NMR		¹³ C NMR
–C(O)CH ₂ CH ₂ CH ₃	0.93	–C(O)CH(CH ₃)CH ₂ –	15.81
–C(O)CH ₂ CH ₃	1.06	–C(O)CH ₂ CH ₂ –	35.75
–C(O)CH(CH ₃)CH ₂ –	1.13	–C(O)CH(CH ₃)CH ₂ –	41.42
–C(O)CH ₂ CH ₃	2.52	–C(O)CH(CH ₃)CH ₂ –	45.21
–C(O)CH ₂ CH ₂ –	2.77		
–C(O)CH(CH ₃)CH ₂ –	2.81	–C(O)CH ₂ CH ₂ –	212.66
–C(O)CH(CH ₃)CH ₂ –	3.15	–C(O)CH(CH ₃)CH ₂ –	214.22
–C(O)C(CH ₃)=CH ₂	6.15	–C(O)CH ₂ CH ₃	217.04

In a typical experiment, [PdCl₂(dppf)] (1.54 × 10^{–3} mmol) was added to 70 mL of H₂O–HCOOH (H₂O = 60 molar % calculated as mol H₂O/(mol H₂O + mol HCOOH × 100)) in the bottle placed in the autoclave. The autoclave was washed by pressurizing with a 1/1 mixture of CO/C₂H₄ (ca. 0.5 MPa) and then depressurizing to atmospheric pressure: this cycle was repeated 5 times, at room temperature. Then 10 mL of liquid propene was added to the reactor containing the catalyst and the H₂O–HCOOH mixture. The autoclave was pressurized with 0.5 MPa of the CO/E mixture and then heated to 90 °C in ca. 10 min without stirring. The pressure was then adjusted to the desired value (typically 4.5 MPa, total pressure by admitting CO and E in the ratio 1/1) while stirring. The pressure was maintained constant throughout the experiment (1 h, stirring rate 700 rpm) by continuously supplying the E/CO = 1/1 monomers. At the end of the experiment the autoclave was quickly cooled and carefully depressurized. GC analysis showed that no light product was formed. The polymer was completely precipitate by addition of 100 mL of H₂O, filtered, washed with water and acetone and dried under vacuum at 70 °C.

The dried polymer was weighted and the productivity was calculated as gPECO/(gPd h).

2.4. Polymers characterization

All the terpolymers have been characterized by IR and NMR spectroscopies. The IR spectra show typical stretching absorptions of CO groups at 1695 cm^{–1} and of –CH₂– groups at 2915 cm^{–1}. Table 1 shows some selected ¹H NMR e ¹³C NMR signals and the assignments are in good agreement with the values reported in literature [34,35].

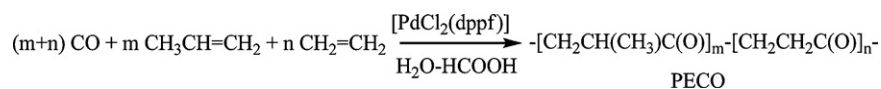
The LVN of a dilute polyketone solution was determined by using the Huggins relationship between the viscosity number and the polymer concentration by extrapolation to zero concentration [36]. The polyketone solution was prepared in *m*-cresol as a solvent and the viscosity was measured by using a Cannon–Fenske type capillary viscosimeter, thermostated at 25 °C.

The *T*_m of terpolymers was determined by the DSC calorimetric curves.

3. Results and discussion

The [PdCl₂(dppf)] complex in H₂O–HCOOH catalyzes the terpolymerization of propene and ethene with CO (Scheme 1) leading to a productivity of 7350 gPECO/(gPd h) under the typical experimental conditions reported in Section 2. This productivity is far superior to the productivity of [Pd(H₂O)₂(dppf)](TsO)₂ in MeOH for the CO–ethene copolymerization [31]. No data have been reported for the terpolymerization with this catalyst. However, it may be foreseen that this catalyst is even less active for the terpolymerization, because it is expected that in the presence of propene the rate of terpolymerization may be slower than that of the CO–ethene copolymerization.

The influence of the H₂O/HCOOH molar ratio, of the amount of liquid propene initially charged and of the reaction time on the



Scheme 1. Reaction of propene and ethene with carbon monoxide to give the polyketone.

productivity, average molecular weight and melting point of the polymer have been studied carrying out the terpolymerization at 90 °C and under 4.5 MPa total pressure, CO/E = 1/1.

3.1. Influence of H₂O concentration

The effect of the addition of H₂O to HCOOH on the productivity has been studied by using a constant initial amount of propene (10 mL). Fig. 1 shows that in pure HCOOH the catalytic activity is very poor. By increasing H₂O concentration, the productivity passes through a maximum of ca. 7350 gPECO/(gPd h) (H₂O = 60 molar %), whereupon a further addition of H₂O causes a significant decreasing of productivity and in pure water the Pd(II) complex becomes practically inactive.

Although it has been reported that in methanol as a solvent both H₂O (in the presence of CO) and HCOOH may efficiently activate the Pd(II) precursor toward the copolymerization and/or the terpolymerization [6,27,37], Fig. 1 shows that [PdCl₂(dppf)] needs the presence of both H₂O and HCOOH in order to reach interesting catalytic activity. As matter of fact, the relative amounts of H₂O and HCOOH determinate the performance of such catalyst probably through a series of cooperative effects: (i) the formation of active Pd(II)–H⁺ species depends on the concentration of both H₂O and HCOOH; (ii) such active species is stabilized by the acid, which prevents deprotonation [22–30]; (iii) the solubility of Pd(II)–dppf, ethene and CO increases by increasing the HCOOH concentration; (iv) the polarity of the H₂O–HCOOH reaction medium contributes on the stabilization of the cationic intermediates formed during the reaction (see mechanism).

At H₂O lower than 60 molar %, the productivity increases probably favored by the higher solubility of monomers (point iii) and by the cooperative effects of H₂O and HCOOH in the formation and stabilization of the active Pd(II)–H⁺ species (points i and ii).

At H₂O higher than 60 molar %, the drop in polymer productivity could be a consequence of the decrease of the reaction rate caused by the lowering of monomers solubility. In addition, under critical

Table 2

Influence of amount of liquid propene initially charged in the autoclave on the productivity, on the LVN, on the *T_m*, and on the % of propene in the polymer chain.

Propene (mL) ^a	Productivity (gPECO/(gPd h))	LVN (dL/g)	<i>T_m</i> (°C)	Propene (mol%) ^b
0	16,500	0.51	256	–
5.0	9500	0.45	211	5.60
10.0	7350	0.35	208	5.65
19.0	4100	0.29	205	5.95
21.5	3560	0.25	203	6.00
26.0	3260	0.20	192	7.00
28.0	2800	0.16	180	7.90
33.5	2300	0.15	179	8.10
37.0	2200	0.11	177	8.30

Run conditions: [PdCl₂(dppf)] = 1.54 × 10^{−3} mmol, H₂O = 60 molar % (calculated as in Fig. 1), *T* = 90 °C, *P_{tot}* = 4.5 MPa, reaction time = 1 h.

^a Liquid propene initially charged into the autoclave.

^b Mol% of propene incorporated in the polymer defined as [mol PCO/(mol PCO + mol ECO)] × 100.

reaction conditions, depending by the propene/H₂O/HCOOH ratio, a liquid phase separation may occur with a consequent drop in the catalytic efficiency, which leads to the decrease of productivity.

3.2. Influence of the amount of liquid propene initially charged

In a set of experiments, carried out to evaluate the influence of H₂O concentration when the initial liquid propene is increased up to 37 mL, the highest productivity is reached always when H₂O concentration ranges between 50 and 65 molar %. On the light of these findings, we have deeply studied at H₂O = 60 molar % the influence of the amount of liquid propene initially charged on the productivity, on the Limit Viscosity Number (LVN) and on the melting temperature (*T_m*).

Fig. 2 shows that by increasing the amount of liquid propene the productivity quickly decreases from ca. 16,500 gECO/(gPd h) in the absence of propene (ECO is produced in this case), down to ca. 2200 gPECO/(gPd h), when 37 mL of propene were charged. Table 2 shows that the LVN and the *T_m* of the terpolymers decrease from

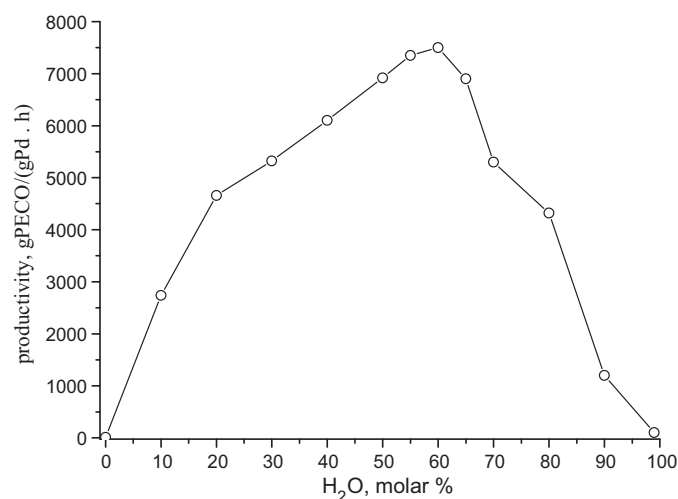


Fig. 1. Influence of H₂O concentration {H₂O % is calculated as: [(mol H₂O)/(mol H₂O + mol HCOOH)] × 100} on the productivity. Run conditions: [PdCl₂(dppf)] = 1.54 × 10^{−3} mmol, liquid propene initially charged = 10 mL, initial volume of HCOOH–H₂O = 70 mL, 90 °C, 4.5 MPa (CO/ethene = 1/1), 1 h.

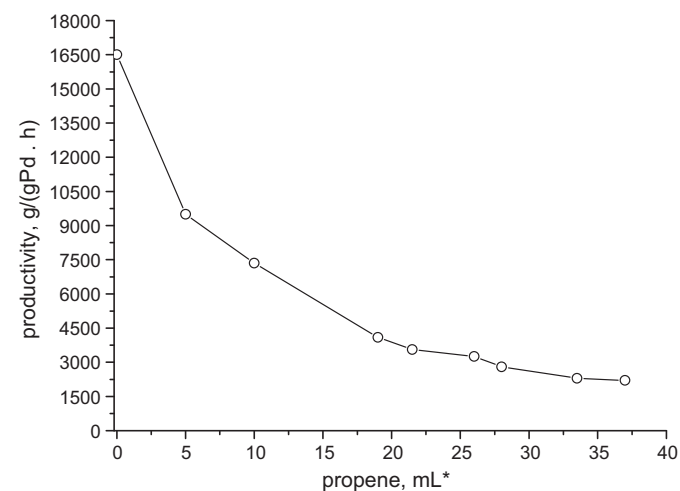


Fig. 2. Influence of amount of liquid propene initially charged in the autoclave on the productivity. Run conditions: [PdCl₂(dppf)] = 1.54 × 10^{−3} mmol, H₂O = 60 molar % (calculated as in Fig. 1), *T* = 90 °C, *P_{tot}* = 4.5 MPa, reaction time = 1 h.

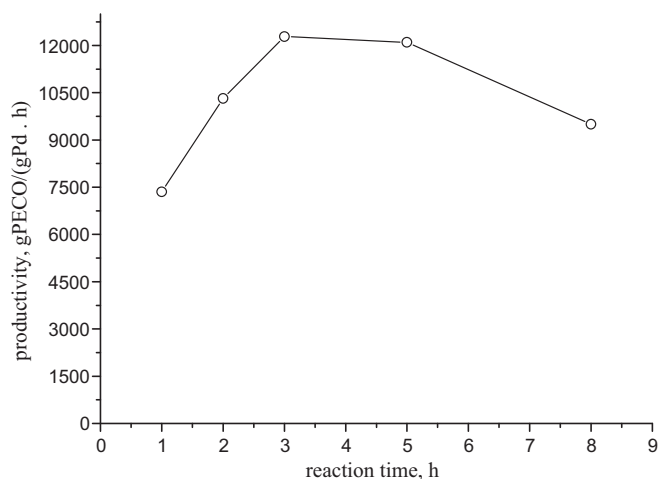


Fig. 3. Influence of the reaction time on the productivity. Run conditions: $[\text{PdCl}_2(\text{dppf})] = 1.54 \times 10^{-3}$ mmol, liquid propene initially charged = 10 mL (see Fig. 2), $\text{H}_2\text{O} = 60$ molar % (calculated as in Fig. 1), initial volume of $\text{HCOOH}-\text{H}_2\text{O} = 70$ mL, 90°C , 4.5 MPa.

0.51 dL/g and 256°C (in the absence of propene) down to 0.11 dL/g and 177°C , when 37 mL of liquid propene were charged. The correlation between melting points and % propene incorporated into PECO is in good agreement with literature data [25]. The amount (mol %) of the propene incorporated has been estimated from the integration of the characteristic PCO and ECO signals in the ^1H NMR spectra [38].

These findings show that propene incorporation is much slower than that of the ethene one, accordingly to what has been reported for catalysts used in MeOH [6,39,40]. In addition, the trend of LVN suggests that as the amount of incorporated propene increases the ratio (rate of chain propagation)/(rate of chain termination) decreases. The decrease of the melting temperature of the terpolymer with respect to the melting temperature of the copolymer ECO (256°C) is also a consequence of the increasing concentration of PCO units in the polymer chain (Table 2).

3.3. Influence of the reaction time

The effect of reaction time on productivity, T_m and LVN has been studied under the reaction conditions of the maximum of productivity reported in Fig. 1 (H_2O 60 molar %, liquid propene initially charged 10 mL).

Fig. 3 shows that by increasing the reaction time, the productivity passes through a maximum of 12,300 gPECO/(gPd h) at ca. 3 h, after that it slightly decreases. Table 3 shows that both LVN and T_m increase progressively with the reaction time.

In order to rationalize the increase of productivity observed in the period from 1 h to 3 h we have to consider that during the reaction, due to the polymer's morphology buildup, the catalysis changes from predominantly homogeneous, in the initial phase (say 1 h), to predominantly heterogeneous (with different cat-

Table 3
Influence of reaction time on the productivity, on the LVN and on the T_m .

Time (h)	Productivity gPECO/(gPd h)	LVN (dL/g)	T_m ($^\circ\text{C}$)
1	7350	0.35	211
2	10,320	0.38	215
3	12,286	0.41	231
5	12,100	0.45	233
8	9500	0.49	238

Run conditions: $[\text{PdCl}_2(\text{dppf})] = 1.54 \times 10^{-3}$ mmol, liquid propene initially charged = 10 mL (see Fig. 2), $\text{H}_2\text{O} = 60$ molar % (calculated as in Fig. 1), initial volume of $\text{HCOOH}-\text{H}_2\text{O} = 70$ mL, 90°C , 4.5 MPa.

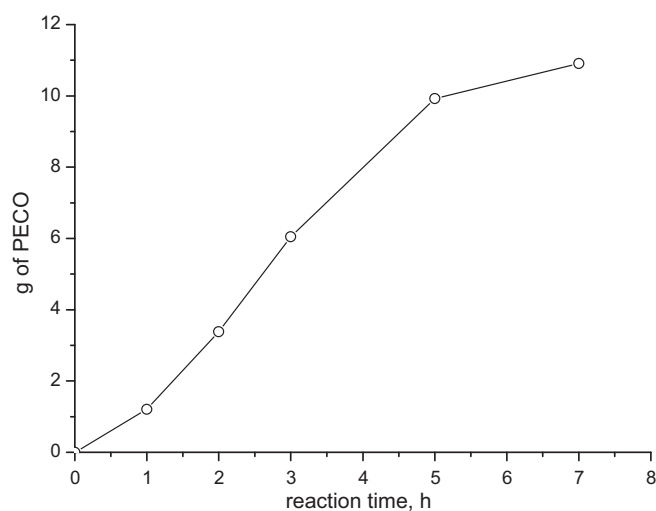


Fig. 4. Amount of polymer formed during the reaction. Run conditions: $[\text{PdCl}_2(\text{dppf})] = 1.54 \times 10^{-3}$ mmol, liquid propene initially charged = 10 mL (see Fig. 2), $\text{H}_2\text{O} = 60$ molar % (calculated as in Fig. 1), initial volume of $\text{HCOOH}-\text{H}_2\text{O} = 70$ mL, 90°C , 4.5 MPa.

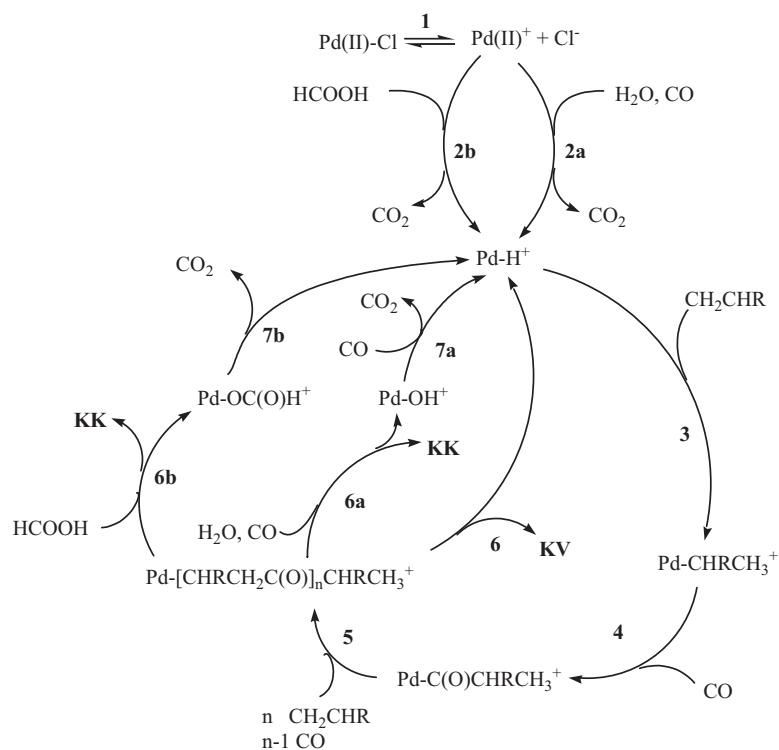
alytic characteristics, propagation/termination, propene vs. ethene reactivity etc.) after 1 h or 3 h, depending on the polymer slurry concentration and bulk density, as the amount of polymer increases in this 3 h period [3]. For longer reaction time, we have to consider that the increase of the slurry concentration makes the stirring less and less efficient. The diffusion of monomers to the active sites probably becomes a determinant factor under these reaction conditions which leads to the decrease of productivity shown in Fig. 3. Indeed, at the end of the reaction we found that most of the solvent is practically incorporated into the polymer. This is better evidenced in Fig. 4 that shows that the increase of the amount of the polymer (g) slows down at reaction times higher than 3 h.

The increase of T_m of the polymers obtained by increasing reaction time further supports the previous suggestion. The T_m of PECO is lower than T_m of ECO, due to the presence of PCO units in the polymer chain. This fact suggests that the increase of T_m in Table 3 at high reaction times may be due to the formation of polymer chains which have a decreasing concentration of PCO units along the polymer chains. At the same time both productivity and LVN increase, because of the increasing of the rate of formation of the ECO units with respect of that of the PCO units. In addition, the linear increase of LVN further suggests that the polymer chain growing process proceeds at rate higher than termination ones also under diffusion control.

3.4. Proposed catalytic cycle

The NMR analysis of the polymer composition indicates the presence along the chain mainly of ECO units together with a low percent of PCO units. Table 1 shows the ^1H NMR (2.77 ppm) and the ^{13}C NMR (35.75 and 212.66 ppm) signals relative to the ECO units, and the ^1H NMR (1.13, 2.81, and 3.15 ppm) and the ^{13}C NMR (15.81, 41.42, 45.21, and 214.22 ppm) signals relative to the PCO units. The end-groups analysis has been performed by the ^1H NMR (signals at 1.06, 2.52 and 6.15 ppm) and the ^{13}C NMR (signal at 217.04 ppm) signals which shows the presence of $\text{CH}_3\text{CH}_2\text{CO}-$ end-groups together with a low percent of the $-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$ vinyl end-groups, whereas neither $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}-$ nor $\text{CH}_3\text{CH}(\text{CH}_3)\text{CO}-$ end-groups have been detected.

The mechanism proposed in literature for the olefin/E/CO terpolymerization by palladium catalysis closely resembles that proposed for olefins/CO copolymerization [1–19].



where:
 R = H or CH₃; **KK** = H-[CHRCH₂C(O)]_nCHRCH₃; **KV** = [CHR=CHC(O)]_nCHRCH₃

Scheme 2. Proposed catalytic cycle.

In the present work the precursor is [PdCl₂(dppf)], but since it is well known that water is capable of coordinating Pd(II) with the formation of aqua-complexes and also that the monomers are capable to coordinate Pd(II) [41,42], it is plausible to suppose that [PdCl₂(dppf)] undergoes equilibrium 1 (Scheme 1) [28,43]. Upon increasing the concentration of H₂O, the formation of a cationic aqua-complex is favored also by the increasing of the dielectric constant of the reaction medium, which favors the separation of the charges. A Pd(II)-aqua-species is not a polymerization initiating species, but upon reacting with CO it can be transformed into an active Pd-H⁺ species through a reaction strictly related to the Water Gas Shift [44–46] (step 2a). HCOOH may also activate the precursor through formation of a Pd-OC(O)H⁺ species followed by β-hydride elimination and evolution of CO₂ (step 2b). In addition, the acid may enhance the concentration of active Pd-H⁺, because it may prevent the deprotonation of the hydride to inactive Pd(0), and hence improving the productivity [23–31].

In the initiation step the olefin inserts into the Pd-H bond with formation of a Pd-alkyl intermediate (step 3) [37,47–50].

The process of chain growing involves alternating reversible CO insertions and irreversible olefin insertions into the Pd-alkyl (Pd-CH₂CHR-Polymer, R=H, CH₃) and into a Pd-acyl (Pd-C(O)CH₂CHR-Polymer, R=H, CH₃) bond, respectively (steps 4 and 5). The composition of the terpolymer chains is ruled by the relative rate of the insertion of the two olefins into the Pd-acyl bond [3,51,52]. The perfectly alternating insertions are due to kinetic and thermodynamic reasons [1–25,53,54].

The high activity may be due to the possibility that the acid prevents deprotonation/dimerization of the active hydride with formation of less active species, thus ensuring a relatively high concentration of the most active species. Moreover, the acid might destabilize the β- or γ-chelates which are formed during the chain growing process through protonation of the oxygen atom

of the coordinating keto group, thus favoring the insertions of the monomers [43].

All the proposed chain transfer polymer forming steps regenerate (directly or after reaction with CO) the active Pd-H⁺ species, which start another catalytic cycle (Scheme 2).

In principle, two chain terminations pathways are possible: i) protonolysis, which involves a Pd-CH₂CHR-C(O)polymer species (Pd-alkyl intermediate) and H₂O [28] (step 6a) and/or HCOOH¹ (step 6b). Protonolysis with H₂O gives the **KK** terpolymers and the Pd-OH⁺ species which inserts CO to form the Pd-COOH⁺ intermediate: the latter gives the active species Pd-H⁺ by elimination of CO₂; ii) termination by β-hydrogen elimination (step 6) which involves a Pd-CH₂CHR-C(O)Polymer species to form **KV** (**V** = vinyl) terpolymers and the Pd-H⁺ active species.

Actually, it is known that protonolysis involves a pre-equilibrium of a β-chelate species with its enolate isomer by a β-H elimination/hydride migration and protonation to the more nucleophilic oxygen atom to give an enol, which rearranges to the ketone [55]. Termination by protonation of this enolate finally produces the ketone-terminating end-group and a Pd-OH⁺ or a Pd-OC(O)H⁺ species, which are converted to active Pd-H⁺ via a partial water gas-shift reaction (step 7a) or a β-H elimination from Pd-OC(O)H⁺ (step 7b).

4. Conclusions

The H₂O-HCOOH solvent composition plays a fundamental role in the activation of the [PdCl₂(dppf)] catalyst precursor toward the terpolymerization of ethene and propene with CO. Such complex was considered poorly active because has strong coordinating lig-

¹ Protonolysis by H₂O has been unambiguously proven [29]. In principle, it cannot be excluded that HCOOH is also responsible of this chain-transfer step.

ands (Cl), but high productivity has been obtained in H₂O–HCOOH as a solvent, when H₂O concentration ranges between 50 and 65 molar %. The productivity, the melting temperature and the viscosity average molecular weight of the terpolymer depend also by the initial propene concentration and by the reaction time. The results and the NMR analysis, however, accord with the formation of a terpolymer having along the chain mainly ethene–CO units together with a low percent of propene–CO units. The end-groups analysis indicates the presence of mainly keto end-groups (CH₃CH₂CO–) together with a low percent of vinyl end-groups.

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